

Thermal Properties of Extruded Injection-Molded Poly(lactic acid) and Milkweed Composites: Degradation Kinetics and Enthalpic Relaxation

Abdellatif A. Mohamed,¹ V. L. Finkenstadt,² D. E. Palmquist,³ P. Rayas-Duarte⁴

¹Cereal Products and Food Science Unit, National Center for Agriculture Utilization Research, USDA-ARS, Peoria, IL 61604

²Plant Polymer Research Unit, National Center for Agriculture Utilization Research, USDA-ARS, Peoria, IL 61604

³National Center for Agriculture Utilization Research, USDA-ARS, Peoria, IL 61604

⁴Food and Agricultural Products Research Center, Oklahoma State University, Stillwater, OK 74078-6055

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ABSTRACT: To determine the degree of compatibility between poly(lactic acid) (PLA) and different biomaterials, PLA was compounded with milkweed fiber, a new crop oil seed. After oil extraction, milkweed remaining cake retained approximately 10% residual oil, 47% protein, and 10% moisture. The fiber (300 μm) was added at 85 : 15 and 70 : 30 PLA : Fiber and blended by extrusion (EX) followed by injection molding (IM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used for testing the composites. After melting in the DSC sealed pans, composites were cooled by immersion in liquid nitrogen and aged (stored) at room temperature for 0, 7, 15, and 30 days. After storage, samples were heated from room temperature to 180°C at 10°C/min. The pure PLA showed a glass transition (T_g) at 60.3°C and the corresponding ΔC_p was 0.464 J/g/°C followed by crystallization and melting transitions. The enthalpic relaxation (ER) of neat PLA and composites steadily increased as a function of storage time. Although the presence of fiber had little effect on ER, IM reduced

it. The percentage crystallinity of neat unprocessed PLA dropped by 95 and 80% for the EX and IM, respectively. The degradation activation energy (E_a) of neat PLA exhibited a significant drop in nitrogen environment, whereas increased in air, indicating PLA resistant to heat degradation in the presence of oxygen. Overall, IM appeared to decrease E_a of the composites, whereas milkweed significantly reduced E_a values in nitrogen environment. Enzymatic degradation of the composites revealed higher degradation rate for the EX samples versus IM, whereas 30% milkweed exhibited higher weight loss compared to the 15%. The degradation mechanism was observed by looking at the percent conversion as a function of E_a from the TGA data, where multisteps degradation occurred mostly in air. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 175–184, 2009

Key words: composites; poly(lactic acid); milkweed; TGA; DSC; degradation kinetics; glass transition; Gordon-Taylor-Fox

INTRODUCTION

There is ongoing need and appeal for widening the use of agricultural by-products in biodegradable plastics for the benefit of environmental protection. Public concern stimulated the development of renewable sources of such biodegradable materials (green composites). Poly(lactic acid) (PLA), is a hydrophobic polymer prepared from renewable agriculture-based feed stocks which are fermented to lactic acid and then polymerized. PLA can be

extruded and injection molded and it is biodegradable in soil, compost or water, where the degradation products of PLA are nontoxic to the environment. PLA has mechanical properties comparable to petroleum-based plastics suitable for use in non-durable applications, short term products, or indoor applications, but is currently more expensive than petroleum-based polymers.^{1,2} The use of renewable and biodegradable fillers is desirable to provide cost-competitive polymer composites and can expand the use of PLA. Composites of PLA with reinforcing fibers^{3,4} were developed, including starch,^{5–10} and inorganic fillers.^{11,12}

In recent work, sugar beet pulp, a coproduct of sugar refining and vital wheat gluten, were blended with PLA,^{13–15} where the results showed little effect of the pulp on the enthalpic relaxation (ER) of PLA. Injection molding (IM) was confirmed to reduce degradation activation energy of PLA and the ER. In this work, PLA was blended, extruded, and

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Correspondence to: A. A. Mohamed (a.mohamed@ars.usda.gov).

injection-molded with milkweed. Milkweed (*Asclepias*) is a new industrial oil-seed crop whose fiber (floss) is in the market as a component of hypoallergenic pillows and comforters. Its seed oil contains linoleic and oleic acids.^{12,13} Industrial oils made from milkweed oilseed and alternate oil seeds are valuable in the United States because they may replace imported oils such as castor, palm kernel, and coconut oil. To improve the economical success of new oilseed crops, an effort is being made to use the biomass coproducts in other value-added products such as biodegradable composite materials.

The objectives of this work were to develop new composites by using commercial PLA as the continuous-phase due to its semicrystalline structure and milkweed powder as the filler. The use of milkweed, a by-product of the oil-seed industry, will indirectly increase profitability of the industry. This is consistent with our effort to develop new uses for agricultural commodities or their by products and to further support the effort been made to protect the environment. This work is the third effort to expand the use of agriculture by-products in new composites formulation. This article is focused on the thermal properties of PLA/milkweed composites using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), where another publication by the same authors was accepted by this journal (in press) addressed the mechanical properties of the same composites.

EXPERIMENTAL

Materials

PLA, provided by Dow Cargill (Minneapolis, MN), contained over 90% L-lactide. The average molecular weight was 150,000. The glass transition (T_g) and melting temperature (T_m), determined by DSC, were 61 and 151°C, respectively. Milkweed seeds were provided by the Natural Fiber Corporation (Ogallala, NE) and contained common milkweed (*syriaca*) and showy milkweed (*speciosa*) seeds harvested from cultivated plots and natural stands. Oil was removed by pressing the oilseeds with a pilot scale expeller (French, model L250). After harvesting and removal of oil, milkweed press seed cake retained approximately 10% residual oil. The protein content of the pressed seed cake was 47 and 10% moisture content. The pressed seed cake was ground and passed through a 300 μm screen.

Extrusion processing

Blending was carried out by a Werner-Pfleiderer ZSK30 corotating twin-screw extruder (Coperion Corporation, Ramsey, NJ). The barrel consisted

of 14 compartments, giving a length/diameter ratio of 44 : 1. The screw speed was 130 RPM and its configuration was reported earlier.¹³ PLA was fed into barrel section 1 using a gravimetric feeder (Model 3000, AccuRate, Whitewater, WI). The oil seed powder was added to the melted PLA in the seventh compartment using a loss-in-weight feeder at a feeding rate of approximately 75 g/min. The extruder barrel was heated using eight heating zones. The temperature profile was 135°C (Zone 1), 190°C (Zone 2), and 177°C (Zones 3–8). A die plate with two holes (4 mm diameter) was used. The melt temperature of the extrudate at the die was approximately 160°C, whereas the residence time was approximately 2.5 min. Die pressure and torque were allowed to stabilize between formulations before sample was collected. Composites-strands were pelletized using a laboratory (2 in.) pelletizer (Killion Extruders, Cedar Grove, NJ).

An ACT75B injection-molder (Cincinnati Milacron, Batavia, OH) was used to produce ASTM D638-99 Type I tensile bars (Master Precision Mold, Greenville, MI) as described in previous work.¹³ Barrel temperature profiles had to be adjusted to help forward material (by cooling the feed section). To allow samples with high milkweed content to cool, the cooling time was increased relative to the neat PLA content.

Aging study

Neat PLA, EX, IM, and PLA-milkweed composites (85 : 15, 70 : 30) were prepared for aging by heating (melting) up to 200°C (10°C/min) in stainless steel DSC pans and cooled by immersion in liquid nitrogen. The pans were then stored at room temperature for 0, 7, 15, and 30 days. The effect of aging was measured by determining the enthalpic relation of PLA.

Enzyme degradation

Extruded injection-molded composites were cut to similar dimensions (10 mm wide \times 10 mm long \times 3.5 mm thickness).¹⁶ Enzyme buffer, 0.05 M Tris-HCl pH 8.6, was prepared (dissolve 0.91 g Tris in 150 mL Millipore water and adjusted to 8.6 using 1 N HCl). Proteinase-K enzyme solution (150 mL) was prepared by dissolving 60 mg enzyme, containing 7.5 unit/mg solid, in addition to 30 mg sodium azide. Each sample (four pieces each) was immersed in 5 mL of enzyme buffer and stored at 37°C with occasional shaking. After 24 h, the enzyme solution of each sample was replaced with fresh buffer to maintain maximum enzymatic activity. After 72 h storage, samples were rinsed with distilled water, and dried under vacuum for 24 h. The difference in

weight before and after enzyme treatment was recorded as percent weight loss. Dried and enzyme-treated samples were mounted onto aluminum specimen holders with silver paint (Fullman, Latham, NY) and were coated under vacuum with gold-palladium at 200/min in a BLANK sputter coating unit. The samples were then observed and photographed in scanning electron microscope (JEOL JXM 6400, JEOL, Tokyo, Japan) at 10 KV.

Differential scanning calorimetry

DSC measurements were performed using a TA DSC™ 2920 (TA Instruments, New Castle, DE). Composites were ground into powder using a Brinkmann/Retsch high-speed shaker mill.¹⁵ Powdered sample (~ 50 mg) was loaded in a stainless steel pan, and the pan was then sealed. Immediately after loaded on the DSC, samples were equilibrated at 0°C, after which the temperature increased at 10°C/min to 200°C. An isotherm (temperature remain unchanged) was maintained for 1 min and samples were cooled to -70°C at 10°C/min. In addition to the PLA:milkweed 85 : 15 and 70 : 30, three more composites (93 : 7; 81 : 19; 55 : 45) were prepared to carry out the Gordon-Taylor-Woods and Kwi equation^{17,18} models for the best possible predictive fit.

Thermogravimetric analysis

The thermal degradation of the composite was performed using TGA 2050 (TA Instruments). Powdered Samples (~ 10 mg) were heated from room temperature to 800°C using 10°C/min and held at an isotherm for 3 min. From the TGA profile, the degradation peak temperature and the weight loss were obtained.

The TGA data was also used to determine the degradation kinetics of the composites by heating each sample at three different rates: 10, 15, and 20°C/min in nitrogen or air. The degradation kinetic was determined¹⁹ using the TA Specialty Library software with reported activation energies at 50% conversion (degradation conversion) based on the Flynn-Walls eq. (1):

$$\log \beta \cong 0.457 \left(-\frac{E_a}{RT} \right) + \left[\log \left(\frac{AE_a}{R} \right) - \log F(a) - 2.315 \right] \quad (1)$$

where β is the heating rate, T is the absolute temperature, R is the gas constant, a is the conversion, E_a is the activation energy, and A is the pre-exponential factor. According to this equation, the E_a can be obtained from the slope of the plot of $\log \beta$ versus $1000/T$ (K) for each percent conversion per minute.

Statistical analysis

Single-factor, mixed model analysis of variance (ANOVA) was used to examine the percent weight loss differences, resulting from enzymatic degradation, between composites for each extrusion (EX) treatment. The fiber ratios were used as replications in the analyses. If the composite effect from an ANOVA F-test statistic was significant at $P < 0.05$, differences of least squares means were used to determine which composites were different from the others. Determination was also made whether any weight loss estimate for a particular composite was significantly different from zero for each EX treatment (i.e., if % weight loss not significantly different from zero, then no weight loss occurred). All analyses were performed using PROC MIXED in SAS® PC for Windows version 9.1.3.

Multiple regressions was used to analyze the DSC data of the composites. The experiment consisted of two PLA/milkweed composites: three fiber ratios: 0 (neat PLA), 15, and 30; four different ageing times: 0, 7, 15, and 30 days; two EX methods: extruded and extruded-injection molded. Five dependant variables (Y_i) were examined: T_g Midt (T_g middle temperature), $T_g \Delta C_p$ (J/g/°C), EX ER ΔH (ER of extruded), ΔH_c (crystallization value J/g), ΔH_m (melting value J/g). For each composite, 40 regression equations of the dependent variables as a function of fiber ratio were obtained [$5 (Y_i) \times 4$ (ageing) $\times 2$ (EX methods)], totaling 80 equations. Predicted values of the dependent variables were obtained to compare neat (0) and milkweed ratio 15 and 30, for each composite, age, and EX method combination at 95% confidence intervals. Overlapping confidence intervals values indicate insignificant difference from one another. All analyses were performed using TableCurve 2D version 5.00, AISN Software, 2000.

RESULTS AND DISCUSSION

Neat PLA and composites were analyzed for their glass transition (T_g), ER, melting, and crystallization using DSC, whereas degradation kinetics was determined by TGA. To link the biodegradability of composites relative to neat PLA, the effect of degrading enzymes was included in the analysis conditions as well. Polymers undergo changes gradually, for instance rigidity and phase separation, therefore thermal analysis was carried out after storage for a period of time. A typical DSC profile of PLA has a glass transition (T_g) followed by crystallization and immediate melting. The parameters of this profile are influenced by the processing conditions, such as EX or IM. The composites were prepared by mixing PLA and milkweed at 0, 15, and 30% milkweed and stored at room temperature for 0, 7, 15, and 30 days

TABLE I
Effect of Milkweed Level and Storage on the Dependant Variables: T_g , Crystallization, and Melting Temperature of Extruded PLA-Milkweed Composites

0 Day		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	54.98 b	0.471 a
15	55.02 a	0.450 b
30	53.30 c	0.388 c
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	24.98 a	25.97 a
15	22.14 b	23.05 b
30	17.39 c	18.18 c
7 Days		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	55.77 a	0.54 a
15	56.08 a	0.51 b
30	57.00 a	0.47 c
% Milkweed	Crystallization ΔH	Melting ΔH (J/g)
0	00.00 ^a	00.00
15	23.64 a	24.19 a
30	19.28 b	19.62 b
15 Days		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	0.00	0.54 a
15	58.01 a	0.53 b
30	58.46 a	0.46 c
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	00.00	00.00
15	24.82 a	25.73 a
30	20.24 b	20.88 b
30 Days		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	00.00	0.53 a
15	58.62 a	0.53 a
30	56.98 b	0.50 b
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	00.00	24.58 a
15	25.34 a	24.57 a
30	20.68 b	23.02 b

The table is based on regression analysis where values within the column followed by the same letter are not significantly different based on non-overlap of 95% confidence intervals. Means within column and storage days with no letters are not significantly different ($a > b > c$).

^a Unobtainable estimate.

before analysis. The outcome of the DSC analyses is shown in Tables I and II, where the T_g and the ΔC_p in addition to the peak temperature of crystallization and melting were listed. Tables I and II represent the EX and IM composites, respectively. It is important to point out here the absence of T_g or crystallization/melting peaks at the 0% milkweed (100% PLA) and after 7 days storage, where values were shown as zero (Tables I and II). Although, there was a very small signal around glass transition area, but it was too small for integration using the software provided by the DSC manufacturer. Possibly, the small signal was due to slow cooling after EX, where

most PLA crystallized and very little remained amorphous. Fast cooling is known to prevent polymer-crystallization and the opposite is true. This phenomena was noticed after both, EX and IM processes. The presence of milkweed significantly reduced the ΔC_p values after storage for 0 and 7 days. Overall, the T_g of PLA was significantly reduced by milkweed, whereas the absence of T_g values indicates the effect of the processing conditions on neat PLA. Lower T_g insinuate looser structure (less compact), where the molecules are further

TABLE II
Effect of Milkweed Level and Storage on the Dependant Variables: T_g , Crystallization, and Melting Temperature of Extruded-Injection Molded PLA-Milkweed composites

0 Day		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	60.63 a	0.47 a
15	56.16 b	0.45 b
30	54.41 c	0.39 c
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	3.51 b	00.00 ¹ b
15	20.95 a	20.92 a
30	20.95 a	21.93 a
7 Days		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	56.71	0.532 a
15	56.71	0.517 b
30	56.85	0.470 c
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	00.00	00.00
15	25.03 a	24.19 a
30	20.08 b	19.61 b
15 Days		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	59.35 a	0.524 a
15	58.11 b	0.519 b
30	57.59 c	0.500 c
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	00.00	00.00
15	24.82 a	25.73 a
30	20.24 b	20.88 b
30 Days		
% Milkweed	T_g (°C)	ΔC_p (J/g/°C)
0	00.00	0.546 a
15	58.54	0.539 b
30	58.84	0.532 c
% Milkweed	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0	00.00	00.00
15	27.24 a	25.79 b
30	22.63 b	26.05 a

The table is based on regression analysis where values within the column followed by the same letter are not significantly different based on non-overlap of 95% confidence intervals. Means within column and storage days with no letters are not significantly different, where $a > b > c$.

^aUnobtainable estimate.

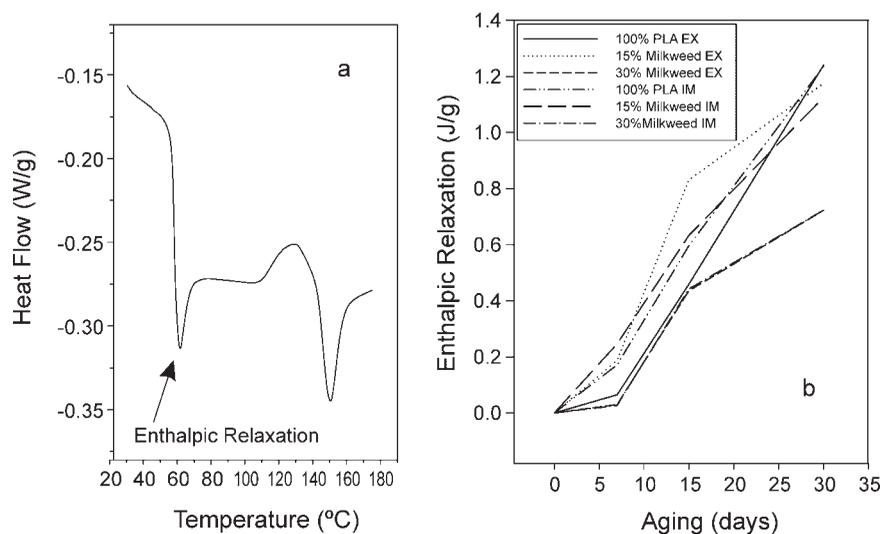


Figure 1 (a) Example of enthalpic relaxation of neat PLA after aging for 30 days; (b) effect of aging on the enthalpic relaxation of extruded and extruded-injection molded PLA-cuphea composites.

apart compared to the neat polymer. Looser structure permits sooner molecular mobility. The looser structure can be attributed to the dilution of PLA by the presence of milkweed. The ΔH of crystallization and melting of the EX was reduced at higher milkweed content and longer storage time. The T_g of neat IM PLA was higher than the EX indicating physical interaction between the two polymers. The ΔH of crystallization and melting was significantly reduced at higher milkweed percentage of the IM composites (Table II). As mentioned earlier, this is due to fast cooling rate of the composites after IM. In general, the T_g of the IM was higher than the EX because the IM samples are more compact due to the molding process, whereas the EX samples are loose thus require lower temperature to reach glassy state. This had little effect on the ΔC_p of neat PLA or composites because the amount of molecules in the amorphous state was unchanged. The presence of milkweed and the storage time had enormous effect on the ΔH of crystallization and melting. After 0 storage time, the IM neat PLA exhibited 3.51 (J/g) while 15% milkweed raised that to 20.95 (J/g) (Table II). It is possible that milkweed as well as storage time assisted PLA molecules in forming bigger and more compact crystals by slowing the cooling rate after IM. We have seen similar PLA behavior in the presence of other fibers.¹⁵

DSC was also used to determine the physical aging of PLA. Since processed-polymer aging is closely related to their cooling rate after processing, powdered samples were melted in DSC pans and quench-cooled by immersion in liquid nitrogen and tested after 0, 7, 15, and 30 days at room temperature. PLA aging was monitored by looking at changes in the T_g and the presence of ER (enthalpic

recovery). ER is a state of the polymer around the glass transition area and signified by a deep endothermic-like transition which indicates that molecules are moving to equilibrium in terms of energy (thermodynamically). As amorphous or semiamorphous polymers quench-cooled and stored below T_g , they tend to move closer to equilibrium state where enthalpy loss will be observed.²⁰ The existence of this state can be determined by re-heating the samples pass T_g , where the recovered enthalpy will appear as an endothermic transition under the T_g (Fig. 1a). Since ER is time dependent, the ER of neat PLA and the composites was not detected after zero storage time, whereas after longer storage time ER had increased constantly. Figure 1b illustrates the increase in ER of the EX composites as a function of storage time relative to neat PLA, where the presence of milkweed and the effect of processing (EX vs. IM) were obvious. At the beginning of the storage time, IM increased the ER, but that effect decreased after 15 days storage (Fig. 1b). The other EX composites continued to show higher ER after 30 days including the neat PLA. In the presence of 15 and 30% milkweed, the IM composites exhibited same ER values, indicating no effect of milkweed level in IM composites. In other words, IM had brought PLA molecules closer, thus they relaxed independent from milkweed content. The 15% milkweed EX composite showed the highest ER values compared to the neat PLA and the other composites. After 30 days, all samples showed similar ER values except for the IM composites where the ER was significantly low (Fig. 1b). This signifies that the molecules reached the lowest energy state possible after 30 days based on the composite formulation and processing conditions. The ER reported in the

TABLE III
Degradation E_a (in Air and Nitrogen), % Crystallinity, and % Weight Loss after Enzymatic Treatment of Neat PLA, and PLA-Milkweed Composites

Sample	Ratio ^a	Process	E_a (air) ^b K.J/mol	E_a (N ₂) ^c K.J/mol	% Crystallinity	% Weight loss ^d
Neat PLA	0	Unprocessed	143.0	218.3	22.7	7.0
Neat PLA	0	Extruded	195.7	183.1	0.75	0.5
Neat PLA	0	Injection molded	165.0	163.5	4.31	1.4
PLA/Milkweed	15	Extruded	170.1	128.0	0.00	3.3
PLA/Milkweed	15	Injection molded	159.0	126.7	1.18	0.7
PLA/Milkweed	30	Extruded	286.5	153.5	0.00	4.2
PLA/Milkweed	30	Injection molded	222.1	190.6	0.69	1.3

^a Ratio of PLA : Fiber.

^b E_a = degradation activation energy in air.

^c E_a = degradation activation energy in nitrogen.

^d weight loss after enzymatic treatment.

literature for neat PLA reached plateau after 6 days storage.¹⁶ In situations like this, the disagreement is caused by the difference in the source of the polymer (PLA in this case) and the cooling rate that takes place immediately after melting and before storage, as well as the sensitivity of the instrument used in the analysis. For instance, if the polymer was cooled at slower rate or had slightly different chemical structure (molecular weight or optical forms D vs. L), that might be a source of variation on the thermomechanical properties. Unlike in the literature, our data showed that ER continued to increase without any indication of reaching a plateau after the 30 days storage.

The degradation activation energy (E_a) of the composites was calculated from the TGA data, where samples were heat-degraded in air and nitrogen environments. The linear form of Flynn-walls equation^{19,21} was used for the calculation, where the slope of the line was the E_a . The equation was based on heating samples at different heating rates and the percent conversion of the material, in the form of weight loss, was determined and recorded after 10% of the material was degraded and continued at a 10% increment. The E_a of neat unprocessed PLA in air was 52% lower than in nitrogen indicating higher instability of PLA in the presence of oxygen. The extruded neat PLA showed much higher E_a in air compared to the unprocessed due to the difference in their thermal history, whereas EX neat PLA samples tested under air exhibited E_a 7% higher than in nitrogen. The EX process helped to stabilize neat PLA in air compared to unprocessed neat PLA. The E_a for the IM neat PLA in air or nitrogen were almost identical (Table III), indicating that IM neat PLA will degrade faster than EX and equally fast in air or nitrogen. In the presence of 15% milkweed, E_a in air for both EX and IM were higher than in nitrogen, but the IM composites showed lower E_a in air. The same trend continued for the 30% milkweed composites but, E_a was much higher for both air and

nitrogen compared to the 15% composite. Overall, E_a for both composites were lower in IM samples than EX. The higher E_a in air environment, possibly, indicates oxidation of biomaterials thus slower degradation, in addition, milkweed contained 10% residual oil and 47% proteins. Oils experience weight increase initially due to the addition of hydrogen at the double bonds causing increase in the sample weight before the beginning of degradation. The plot of E_a as a function of % conversion (TGA degradation conversion) can be used to determine the degradation mechanism, i.e., whether the degradation was a one-step or multistep process.¹⁴ Such a graph is shown in Figure 2 where both degradations in air or nitrogen were represented. In Figure 2a, IM neat PLA degraded in air and nitrogen signify a two-step degradation process. Although, the mechanism appears to be the same, but the E_a at any %conversion was different. The picture was different for the EX neat PLA, where in nitrogen, it was a one-step process and multistep mechanism in air. It is obvious, the effect of processing (EX vs. IM) in addition to the sample composition and the degradation environment on the E_a values. In Figure 2b, composites (30% milkweed only) exhibited multisteps mechanism in air and nitrogen except the IM 30% milkweed in nitrogen exhibited one-step, indicating the effect of degradation-environment was much more pronounced than the process (EX vs. IM). PLA composites with other biomaterials showed a much more obvious role of processing than air versus nitrogen.¹⁴ That could be due to the presence of the residual oil in milkweed. Multisteps were observed for the IM composites with 15% milkweed in air, whereas the data for the EX 15% composite exhibited a one step mechanism (Table IV).

Enzyme activity is often affected by the substrate physical state (viscosity or morphology) because it is closely related to accessibility thus with the enzyme activity. Since the morphology of the tested samples is expected to be different due to EX and IM

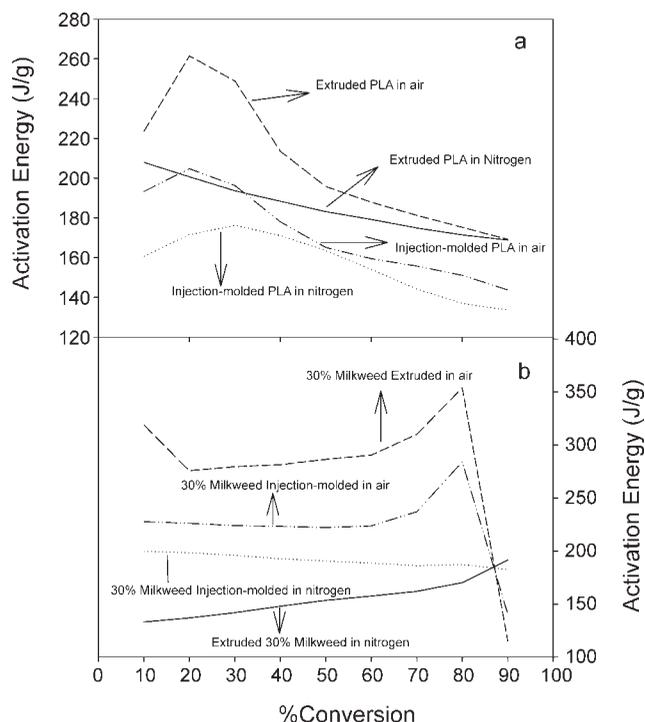


Figure 2 TGA degradation-activation energy of extruded and extruded-injection molded: (a) neat PLA (in air and nitrogen); (b) 30% milkweed (in air and nitrogen) as a function of % conversion.

processes, it is expected that proteinase-K activity will be affected. Samples weight loss was used as indicator of enzyme activity, where higher weight loss indicates elevated activity. Unprocessed neat PLA was the sample with most weight loss, indicating looser physical structure thus higher degradation.

As expected, the EX and the IM samples with much less accessibility for the enzyme, exhibited less degradation with the EX sample being the least available for the enzyme (Table III). The composites behaved differently, where the EX samples were much more degraded than the IM and the presence of more milkweed increased the weight loss. The higher weight loss is attributed to the dilution of PLA by milkweed. The IM composites lost the least weight of all other samples (Table III). The compactness of the IM composites limited the degradation to the surface and the edges of the samples as shown by the scanning electron micrograph images shown in Figure 3. The enzymatic degradation-rate is very important for estimating the relative biodegradability of the composites in comparison to petroleum based composites and to other biopolymers.

The weight loss was also correlated with the % crystallinity of the samples because crystals are more compact and difficult to access. The degree of crystallinity was calculated by subtracting the ΔH of fusion of the material from the ΔH of crystallization and divided by the ΔH of the neat polymer which is 93.6 for PLA.¹⁴ The EX composites exhibited no crystallinity, conversely, the crystallinity of the IM samples for the 15% milkweed samples was higher than the 30% (Table III). Although PLA is semicrystalline polymer, when cooled fast, it turn to 100% amorphous, but it allowed enough time it will form a semicrystalline structure. The 100% amorphous composites were the same samples with the higher weight loss in Table III. The crystallinity of neat unprocessed PLA dropped from 22.7 to 4.31% and 0.75% for the IM and EX respectively. This is

TABLE IV
TGA Degradation E_a of PLA Composites Listed in % Conversion for all Composites Extruded and Extruded-Injection Molded in Air and in Nitrogen

PLA	Ratio ^c	Process	10% ^d	20%	30%	40%	50%	60%	70%	80%	90%
PLA ^a	0	Extruded	207.9 ^e	200.6	193.6	188.3	183.1	179.2	174.9	171.4	168.8
PLA ^a	0	Injection molded	160.6	171.5	176.2	171.0	163.5	154.0	144.1	136.9	133.6
PLA : Milkweed ^a	85 : 15	Extruded	83.9	99.0	110.1	119.8	128.0	135.7	142.7	145.4	143.4
PLA : Milkweed ^a	85 : 15	Injection molded	116.8	120.0	121.2	123.3	126.7	126.9	134.1	138.1	144.5
PLA : Milkweed ^a	70 : 30	Extruded	133.1	136.9	141.9	148.0	153.5	157.6	162.0	170.2	191.6
PLA : Milkweed ^a	70 : 30	Injection molded	199.8	198.4	195.9	192.6	190.6	188.6	186.1	187.2	182.6
PLA ^b	0	Extruded	223.6	261.4	248.8	213.4	195.7	187.8	181.2	175.2	169.1
PLA ^b	0	Injection molded	193.3	204.7	196.2	177.9	165.0	159.4	155.7	151.0	143.7
PLA : Milkweed ^b	85 : 15	Extruded	151.6	157.6	162.7	166.9	170.1	173.6	174.2	176.0	188.3
PLA : Milkweed ^b	85 : 15	Injection molded	144.4	161.6	163.2	161.5	159.0	159.5	162.7	170.7	199.7
PLA : Milkweed ^b	70 : 30	Extruded	318.9	275.8	279.5	281.4	286.5	290.4	310.1	354.1	115.3
PLA : Milkweed ^b	70 : 30	Injection molded	227.7	226.1	224.0	222.1	223.2	223.7	237.0	284.1	140.8

^a TGA test in nitrogen.

^b TGA test in air.

^c Ratio = PLA : Milkweed.

^d The percent degradation conversion of PLA and Milkweed composites.

^e Activation energy (J/g).

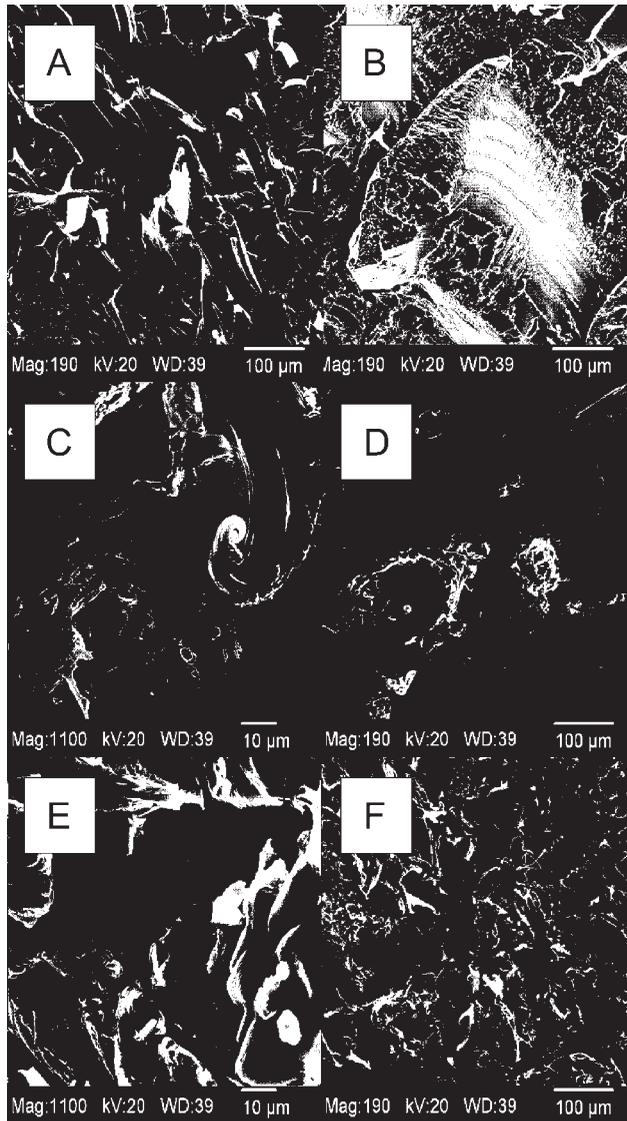


Figure 3 Scanning electron micrograph of extruded and injection-molded PLA and composites, enzymatically treated neat PLA, and PLA-lesquerella composite. (A) EX neat PLA; (B) IM neat PLA; (C) EX 30% milkweed; (D) 30% IM milkweed; (E) enzymatically treated EX 30% milkweed; (F) enzymatically treated IM 30% milkweed.

another proof of the difference in properties between the unprocessed neat PLA and the EX and IM samples prepared for this work. The relationship between % crystallinity and weight loss after enzyme degradation are illustrated in Figure 4. Lower weight loss was associated with crystallinity and with the percentage of milkweed in the composites. The effect of the type of process is apparent in Figure 4, where IM effect on the % crystallinity limited the weight loss whereas the absence of crystallinity in the EX exemplified the effect of milkweed on the composites weight loss. The enzymatic activity as represented by the weight loss could be a good starting point on determining the degree of

biodegradability of these composites. In addition, the type and conditions of processing need to be considered when executing biodegradable studies such as EX or IM, % crystallinity and composites morphology.

Polymers miscibility is often measured by the occurrence of one T_g for any copolymers in a composite.²⁰ Composites qualitative or quantitative characteristics can be obtained from their thermal properties by measuring parameters such as T_g , melting, and crystallization. Polymers inter and intramolecular interactions in and or between molecules will determine their miscibility.²² The intensity of these interactions, which might occur in different forms for instance hydrogen bonding, can be estimated by DSC analysis. Mathematical model equations such as Gordon-Taylor equation (M. Gordon and J. S Taylor) were developed to estimate this interaction and predict T_g of composites with different compositions than the composition of the tested samples.¹⁷ For better fit, the Gordon-Taylor equation²¹ was modified and rearranged to take the Gordon-Taylor-Wood equation (L. A. Wood)²:

$$T_g^b = \frac{W_1 T_{g1} + K(1 - W_1) T_{g2}}{W_1 + K(1 - W_1)} \quad (2)$$

where T_g^b = composite glass transition, W_1 and W_2 = % weight fraction of milkweed and PLA respectively, T_{g1} and T_{g2} = glass transition of milkweed and PLA were 46.0 and 60.3°C respectively, and K = adjustable fitting parameter related to the strength of the interaction between the two components in the composite (miscibility). The K value is unique for each composite and cannot be used for composites with completely different ratios.

The predicted T_g value is represented in Figure 5 and Table V, where five experimental data points

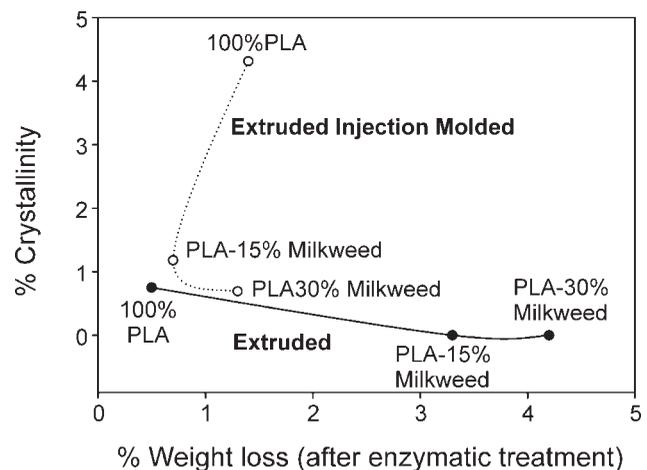


Figure 4 The effect of % crystallinity on the weight loss of neat PLA and PLA-milkweed composites subsequent to enzymatic treatment.

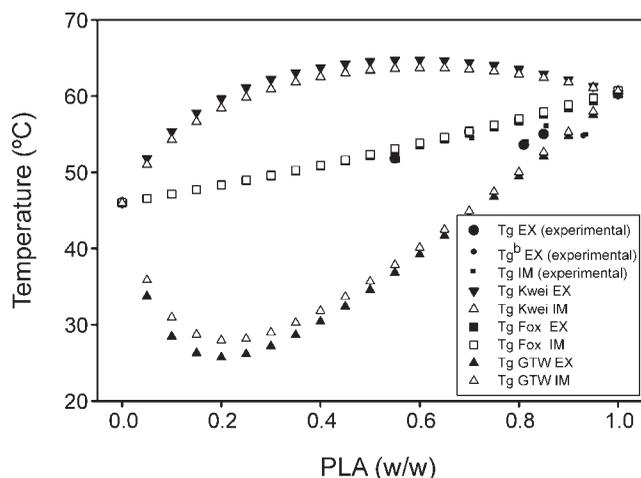


Figure 5 T_g versus composition in PLA-milkweed composite. The predicted T_g values by Gordon-Taylor-Kwei and Fox equations using K and q values listed in Table V. Unlike Gordon Taylor-Wood equation where one T_g value is fixed, the Kwei method uses both T_g values for the best fit.

were used. To estimate the intermolecular interactions between composite components, the Gordon-Taylor equation was modified by Kwei et al.¹⁸ and included a new term (q) regarded as interaction coefficient between components W_1 and W_2 when $W_1 = (1 - W_2)$. In the Kwei eq. (3), both K and q are used in fitting T_g data obtained from DSC. The positive or negative value of q indicates the direction of the T_g -change and its magnitude, which signifies the strength of the net effect on the T_g value due to intermolecular interaction, such as hydrogen bonding.¹⁸

$$T_g^b = \frac{W_1 T_{g1} + K(1 - W_1) T_{g2} + q W_1 (1 - W_1)}{W_1 + K(1 - W_1)} \quad (3)$$

The Fox equation (T. G. Fox)⁵ is one more equation applied for predicting T_g dependence of PLA/milkweed composites and is symbolize as:

$$T_g^b = \frac{T_{g1} T_{g2}}{W_1 T_{g2} + W_2 T_{g1}} \quad (4)$$

The results in Table V indicate the best fit parameters (K and q) for Gordon-Taylor-Wood, Kwei, and

Fox equations. Although all equations listed in Table V have R^2 listed, a K value was listed for both Gordon-Taylor-Woods and Kwei equations and q value for Kwei equation only. The data in Table V indicates that the Kwei equation provided the best fit with $R^2 = 0.94$ for both extruded and injection molded, where $q = 22.53$ and 18.92 for the EX and IM, respectively. The Gordon-Taylor-Wood showed the second best fit ($R^2 = 0.819$ and 0.873) at $K = 0.384$ and 0.368 for EX and IM, respectively. The higher q value (22.53) of the EX samples is indicative of the grater effect of EX on the intermolecular interaction over IM (18.92) (Table V). We can infer from the positive q value that the presence of milkweed did not bring the T_g of the composites below the T_g of the components used in the composite. It is possible for q to have a negative value as in the case of PLA/sugar beet/apple fiber composites.¹⁵ The negative value indicates that the intermolecular interaction was strong enough to bring the T_g of the composite below the T_g of its components (the neat polymers).

CONCLUSIONS

The type of processing (EX vs. IM) and the amount of fiber in the composite are equally important in influencing the thermal properties of the composites. The thermal history of the raw PLA is crucial as well because it is dependant on the manufacturer. Neat PLA showed an increasing ER with aging time. EX had more influence on the ER, degradation activation energy of PLA and composites compared to injection molded. The presence of milkweed significantly decreased the ΔH of crystallization and melting composites of both extruded and injection molded as well as T_g . In the most part, composites heat degradation in air required higher activation energy compared to the nitrogen environment, whereas the activation energy for the extruded composites with 30% milkweed was the highest. Unlike in nitrogen, the activation energy values indicated that composites degradation in air appeared to occur in multisteps for the extruded composites. Neat PLA

TABLE V
Computed K and q Values from T_g^b Data with Best Fit Correlation Coefficients R^2 for Extruded and Injection-Molded PLA Composites

Blend	K	q	R^2
PLA-Milkweed (extruded Kwei)	0.1057	22.5359	0.93964
PLA-Milkweed (injection molded Kwei)	0.1312	18.9262	0.94238
PLA-Milkweed (extruded GTW)	0.3835	-	0.8192
PLA-Milkweed (injection molded GTW)	0.3679	-	0.8733
PLA-Milkweed (extruded Fox)	-	-	0.6694
PLA-Milkweed (injection molded Fox)	-	-	0.7025

The parameters were used in predicting T_g as derived by Gordon-Taylor and Fox.

crystallinity was significantly reduced by IM and further decreased by EX. Extruded composites with 15 and 30% milkweed did not crystallize after EX. The enzymatic degradation of the composites was correlated with the percent crystallinity and thus with the processing (EX or IM) as indicated by the weight loss. Injection molded samples were attacked by the enzyme from the surface and from the edges, whereas the extruded samples were attacked from all direction as shown by the scanning electron microscope. The best fit for T_g prediction of the composites was determined by the Kwei equation at $q = 22.54$ and 18.93 and $K = 0.105$ ($R^2 = 0.93$) and 0.131 ($R^2 = 0.94$) for the extruded and injection molded composites, respectively. The Gordon-Taylor-Wood and Fox equations exhibited lower R^2 at 0.81 (EX) and 0.87 (IM) or 0.67 (EX) and 0.70 (IM), respectively.

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